Photoluminescence study of the synthesized nanomaterials in presence of macromolecules and heavy metal ions

Summary of Research Work for the Award of Ph.D. Degree in Chemistry

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Introduction

Human used tools and techniques for the development of their civilisation. In the early stage of human civilisation, they used stone for prepared their tools. As the time passed away human developed their tools with time and the materials used to prepare the tools also changed to nanomaterials from stone. The modern human civilisation is mainly a nanomaterials based civilisation where nanomaterials is used for the creation and developments of tools. In 2004, Geim and co-workers discovered a new two-dimensional carbon-based nanomaterial, named as graphene. It is basically single layer of sp^2 hybridised carbon atoms with only one atom thickness. Discovery of graphene is opens up a new avenue of modern civilisations due to its unique physical and chemical properties. In modern time graphene and graphene-based nanomaterials have tremendous utilisation in research for developing human tools.

1. 1. Objective of my Work:

- Synthesis of metal incorporated graphene Oxide (GO) based nanoparticles, Graphene oxide derivatives and Carbon based nanomaterials.
- Study of photoluminescence property of newly synthesized nanomaterials.
- Understanding of the role of solvents, macromolecules and heavy metal ions in the synthesized GO based nanomaterial.
- Study of interaction between carbon based nanomaterials (Graphitic Carbon Nitride) and GO

1.2. Overview of the Work:

Graphene is a zero-gap semimetal. Introduction of large number of defect sites originated by the presence of several oxygen containing functional groups on its surface, band gap of graphene is modified [1]. GO, one of such modified graphene sheets, exhibits interesting photoluminescence properties [3-4]. Manish Chhowalla and coworkers [1], X. Sun. et al. [2] and Z. Luo et al. [3] are working on the photoluminescence characteristics of GO. Apart from this, synthesis and band gap modulation of high-quality GO quantum dots provides more research opportunities. Recently, many research groups have attempted to decorate the graphene oxide surface by luminescent rare earth ions complexes or nanoparticles for biomedical applications [5-9] and environmental management [10-11]. Cao et al. have reported an important way for non-covalent attaching of graphene oxide sheets with rare earth

complexes which may be useful in biological lebelling [6]. X. Fan et al. have produced a supramolecular functionalized luminescent GO having biomedical applications by the decoration of GO surface with Sm3+-complexes [8]. GO-rare earth metal-organic framework composites are also found to be useful for the selective isolation and separation of biomolecules [9]. X. Wang and co-workers have demonstrated the application of GO nanosheets for the removal of trivalent lanthanides and actinides from aqueous solutions and this method may be utilized in environmental management [11]. Apart from the research on broad emissive nanomaterials for the applications in biology, solar cells, fiber optics, bioimaging, pollutant sensing, selective detection of explosive aromatic nitro compounds by GO based nanomaterials has drawn tremendous attention in the last few years. In a recent work, Dinda et al. have reported a luminescent reduced GO for the selective detection trinitrophenol, the most common constituent to prepare powerful explosive [12]. These type of studies by using rare earth element complexes are also inspiring us to think about water soluble GO based nanomaterials or quantum dots having very high luminescence intensity for the detection of explosive compounds.

M. R. Das and co-workers have investigated the antimicrobial activity of GO-Ag hybrids materials [13]. Mehmet Lütfi Yola et al have detected Quercetin and Morin simultaneously by an electro analytical nanosensor based on graphene oxide/silver nanoparticles [14]. S. Gurunathan and co-workers have used GO-AgNPOs as neuronal differentiation markers and stem cell markers [15].

Hu and co-workers have used Pluronic F127/graphene nanosheet as a nanocarrier in biomedicine [16]. Sahu et al have reported the formation of a self-assembled hydrogel of graphene oxide nanosheets by physically crosslinking at a low concentration of Pluronic F127 [17]. Yan and co-workers have studied the anchor-buoy-type adsorption of F127 on GO layers resulting single-layer intercalation and the presence of “anchor-buoy-type brush” and clusters of P123 on the GO surface results the variable intercalation. In the anchor-buoy-type configuration, long hydrophobic segments of F127 play the role to form a hydration protection layer to prevent the aggregation of GO sheets [18].

1.3. Plan of the Thesis:

Synthesis and photoluminescence studies of nanomaterials (Graphene oxide based nanomaterials and carbon based nitrogen incorporated nanomaterials) and their interactions with different additives, like, polymer, copolymer, metal ion, will be discussed in the thesis entitled "**Photoluminescence study of the synthesized nanomaterials in presence of macromolecules and heavy metal ions**". The thesis will include following chapters.

Chapter I: Introduction consisting of motivation and objective of the work

Chapter II: An overview on the photoluminescence behaviour of the carbon based nanomaterials along with theoretical studies on the tunable photoluminescence

Chapter III: Photoluminescence Study of Cerium incorporated Graphene Oxide Nanoparticles (GO-Ce NPs).

Chapter IV: Optical sensing by GO-Ce NPs.

Chapter V: Tuning of Photoluminescence of GO Derivatives: Effect of Solvent (Water).

Chapter VI: Effect of Temperature on Photoluminescence of GO-PANI Nanocomposite.

Chapter VII: Photoluminescence of Graphitic Carbon Nitride: Effect of pH and Interaction with GO.

Chapter VIII: Photoluminescence modulation of Graphene Oxide (GO) in presence of Pluronic F-127 Copolymer.

Chapter IX: Conclusion

2. a. Brief description about the carbon based nanomaterials

Chemically derived nano-materials are increasingly attracting researchers for their optical and electrical characteristics. Due to high surface area and structural inhomogeneity, carbon based nanomaterials have tremendous applications in modern science and technology for the development in optoelectronic devices such as light emitting diode, bio-trackers, drug delivery system and sensors of biomolecules, environmentally hazards pollutants and explosive compounds. Presence of several oxygen containing functional groups at the surfaces of the graphene oxide (GO) and GO based nanomaterials obtained from graphite by strongly

oxidative acidic medium, results the increase in the interacting ability with different inorganic, organic or bio-molecules.

2. b. Experimental techniques used for the work

After the synthesis of the nanomaterials, we have characterised them by Raman spectrum, FT-IR spectrum, XPS, X-ray diffraction study, scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Absorption spectra were recorded on a Hitachi U-4010 spectrophotometer at room temperature. The steady state emission and photoluminescence excitation spectra were measured using a Hitachi Model F-7000 spectrofluorometer equipped with a 150W xenon lamp. The life time of the nanomaterials dispersion was measured by using TCSPC from PTI, USA, with the help of sub nanosecond pulsed LED source (280 nm having a pulse width of 600 ps). The pulsed LED source of 280 nm was operated at 10 MHz repetition rate driven by a PDL 800-B driver, Pico Quant, Germany. LED profile was measured at the excitation of 280 nm with a band pass of 3 nm using Ludox as the scatterer. Decay measurements using “magic angle” detection with an emission polarizer set at 54.7° were carried out. The decay parameters were measured using nonlinear iterative fitting procedure based on the Marquard algorithm [19].

3. Summary of the work

3.1. Synthesis of the nanomaterials

Synthesis of GO

Aqueous dispersion of GO was prepared on the basis of modified Hummer's method [17]. Concentrated H_2SO_4 (100 ml) was added to a mixture of graphite flakes (4.0 g) and $NaNO_3$ (1.0 g) and the resulting mixture was stirred continuously at about $0^{\circ}C$ maintained by keeping it in an ice-bath. Then the solid $KMnO_4$ (12.0 g) was stepwise added with the vigorous stirring for 6 hours at $20^{\circ}C$. Next, an additional $KMnO_4$ (12.0 g) was added at a time with stirring for 12 hours at room temperature. Then about 600 ml of ice-cold water and 30% H_2O_2 drop wise added to reduce the excess $KMnO_4$and to stop the further oxidation. The mixture was then purified by washing with 5% HCl and 50% ethanol to isolate GO mass. The obtained mass was dried under vacuum at $60^{\circ}C$ and collected solid brown product.

Synthesis of GO NPs:

On the basis of modified Hummer's Method[18], the preparation of the solid GO was described in Ref. 18b. The solid brown product as pure GO was dispersed in water by sonication and used for spectroscopic study. The GO-NPs was synthesized by the treatment of GO with 1:1 mixture of H_2SO_4 and HNO_3 at 90℃ with constant stirring(1400-1500rpm) for 4-5 hours and the mixture was allowed to cool down to room temperature. The mixture was diluted by ice cold water and neutralized by NaOH solution. Then the solid mass was filtered by Whatmann 42 filter paper. The obtained mass was purified by washing with water and 50% ethanol and dried under vaccum at 60℃.The solid product as pure GO-NPs was dispersed in water by sonication and used for spectroscopic study.

Synthesis of Cerium incorporated GO NPs:

The incubating of cerium ions on the GO NPs was done in one pot. CAN (mass ratio of GO NPs and CAN was 1:1) was added to the mixed acid solution of GO-NPs on same condition, stirring at same rpm speed for 4-5 hours. At this concentrated sulphuric acid medium Ce (IV) of CAN converts partially to Ce (III).[19]Then neutralized filtered (by Whatmann 42

filter paper) was washed with carefully by water and 50% ethanol. The obtained mass was dried under vacuum at 60℃.

Synthesis of OH-enriched GO QD:

On the basis of modified Hummer's Method[18], the preparation of the solid GO was described in Ref. 18b. The solid brown product as pure GO was dispersed in water by sonication and used for spectroscopic study. The OH-GO QD was synthesized by the treatment of GO with 1(N) NaOH solutions at 80^{o}C-90℃ with constant stirring(1400-1500rpm) for 4-5 hours and the mixture was allowed to cool down to room temperature. Then the solid mass was filtered by Whatman 42 filter paper. The obtained mass was purified by washing with only water and dried under vacuum at 60℃.The solid product as pure OH-GO QD was dispersed in water by sonication and used for spectroscopic study.

Synthesis of GO-PANI:

GO-PANI composites have been prepared by the dispersion of aniline (10.2mg, 0.11 mmol) and GO (102 mg, GO: Aniline mass ratio = 10:1) and dispersed in water by sonication. Aqueous solution of ammonium per sulphate (APS, 1.1 mmol) was added very slowly over 30 min and the mixture was allowed to stand for 24 hrs at low temperature. The resultant precipitate was filtered and washed several times with water and methanol. Finally, it was dried under vacuum for 48 hrs at room temperature.

Synthesis of Graphitic carbon nitride:

Graphitic carbon nitride (g-C_3N_4) has been widely used for recent years as it has a very decent use as catalysis and other behaviours. To synthesize this excellent compound, following steps are required, for the synthesis procedure the starting material is Formamide ($HCONH_2$). At first round about 70 ml of formamide is taken in a conical flask. This whole thing then passed through autoclave, where this compound is pressurised. This autoclave process is done about a constant temperature of 180^{0}C about 72 hours. Then this compound is taken from the autoclave and rotatory evaporated at the constant temperature of 180^{0}C.After rotatory evaporation done it is cooled down in a water bath, the liquid compound is formed at the bottom of the conical. This liquid sample then taken cooled down for some times and it is boiled at 100^{0}C constant temperature for a day or more until the whole compound is solidified. At last the final product we get is the polymerised Graphitic carbon nitride.

3.2. Photoluminescence Study

3.2.1. Photoluminescence Study of Cerium incorporated Graphene Oxide Nanoparticles (GO-Ce NPs).

The absorption patterns of GO and GO NPs are almost same (Figure **1**a) and according to previous reports of the UV photoluminescence of GO, the absorption around and below 250 nm is originating from π to π* transition whereas the absorption above 280 nm arises from the n to π* transition. However, GO-Ce NPs possess a different absorpption spectra consisting of a band around 250 nm suggesting the formation of new material by the incorporation of cerium ions within GO NPs. A closer look of this band indicates the existence of two bands, one is around 240 nm and another is at 255 nm which may be due to splitting of F states as a result of spin orbit coupling. Photoluminescence study shows amplification of photoluminescence intensityof GO-Ce NPs100 fold compared to graphene oxide(Figure 1b), the origin of such enhancement of GO-Ce NPs is investigated by exploring binding interaction between cerium ions and GO NPs and the structural orderness of the GO NPs in presence of cerium. The emission spectra of the solution of mixture Ce (III) and Ce (IV) along with a solution of GO and GO NPs separately, reveals the higher emission intensity of GO NPs in presence of cerium ions compared to that of aqueous solution of Ce (III) and Ce (IV) whereas the luminescence intensity in presence of GO is little bit low with respect to the cerium solution(Figure 1c). The photoluminescence spectra of GO-Ce NPs, centered at around 350 nm is deconvoluted into four different emission bands (Figure 1d). This may be attributed to the different locations of the cerium ions. The cerium ions bound within the basal plane of GO moiety are facing relatively less polar environment and the cerium ions present in the outer surface of the GO moiety are facing highly polar environment. Again, as already mentioned, each luminescence band from cerium ions present in the two different locations results two further bands, originated by 5d-$^2F_{5/2}$ and 5d-$^2F_{7/2}$ transitions. The relatively blue shifted bands centered at 339 nm and 353 nm are originating from the cerium ions present within the basal planes surrounded by less polar environment and relatively red shifted bands centered at 367 nm and 384 nm are due to the electronic transitions from excited cerium ions at more polar environment (Figure 1d). Interestingly the excitation spectra collected from the blue shifted emission (345 nm) and red shifted emission (370 nm) does not differ much, concluding same ground state for different types of emissions. This may be because of the inert behavior of the cerium 4f orbital towards the environment. Although the cerium ions present in the different environment, due to this inertness of 4f orbital ground state energy does not differ for different cerium ions. After

photoexcitation the electron goes to the 5d orbital which is much more exposed to the environment, interact with the solvent molecules and relaxed. The 5d orbital of the cerium ions present in the comparatively polar environment relaxes its energy to maximum extent and the red shifted bands are obtained.

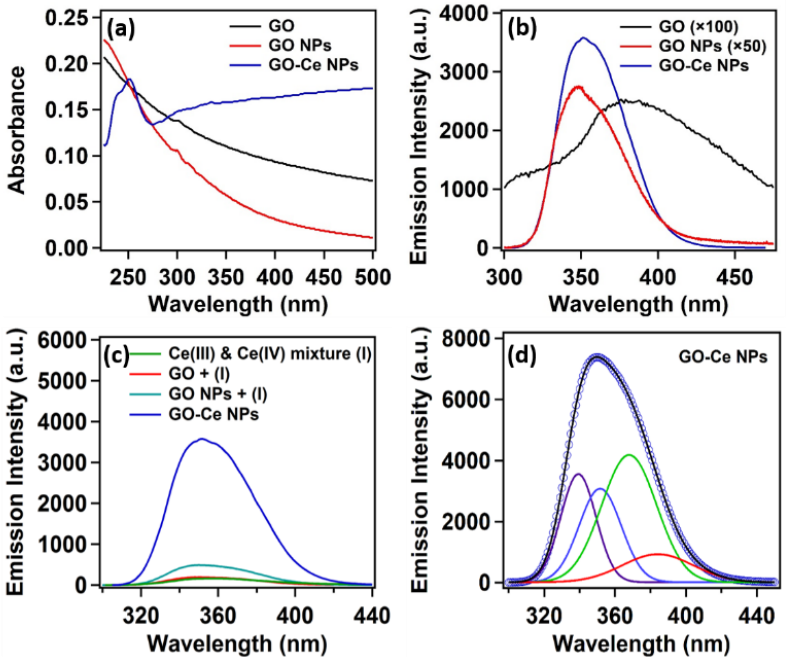

Figure 1. *Steady state spectral analysis of GO NPs and GO-Ce NPs. (a) Absorption spectra of GO, GO NPs and GO-Ce NPs. (b) Emission spectra of GO, GO NPs and GO-Ce NPs. Excitation wavelength is 250 nm. (c) Emission spectra of an aqueous sloution of Ce (III) and Ce (IV) termed as (I), (I) in presence of GO, (I) in presence of GO NPs, and GO-Ce NPs. (c) Deconvoluted emission spectra of GO-Ce NPs.*

Incorporation of cerium into this GO NPs results in quenching of this LW photoluminescence band of GO centered at 520 nm (Figure 2a). To investigate the actual reason behind this quenching of photoluminescence band, excitation spectra of both GO NPs and GO-Ce NPs have been collected at 520 nm (Figure 2b). Excitation spectra of GO NPs at 520 nm shows a broad peak from 425 nm to 480 nm which is mainly due to the strong and extended coupling of the oxygen containing functional groups. Cerium incorporation into the GO NPs (GO-Ce NPs) highly altered the excitation spectra which conclude the different nature of ground state. The diminishing of broad character the excitation spectra after cerium

incorporation and very sharp peaks at around 400 and 440 nm may be attributed to the absence of extended coupling between the oxygen containing functional groups. This phenomenon can be related directly to the Raman spectra suggesting the structural change of GO NPs which includes the reducing of the defect states by forming a ordered structure involving oxygen functionalities through cerium ions. This eventually restrict the direct overlap of the orbitals related to the functional groups. So the restriction in coupling between oxygen containing functional groups is the main reason behind the quenching of the luminescence band at 520 nm in GO-Ce NPs. The time resolved photoluminescence spectra (Figure 2c) further gives us the mechanistic over view of this quenching process. As the incorporation of cerium ions results the disappearance of all radiative recombination channels, the relative contribution of the subnanosecond component becomes almost 100% which is clearly pointing outthe activation of nonradiative decay channel because of photoinduced reduction of Ce (IV) through the oxygen containing functional groups.

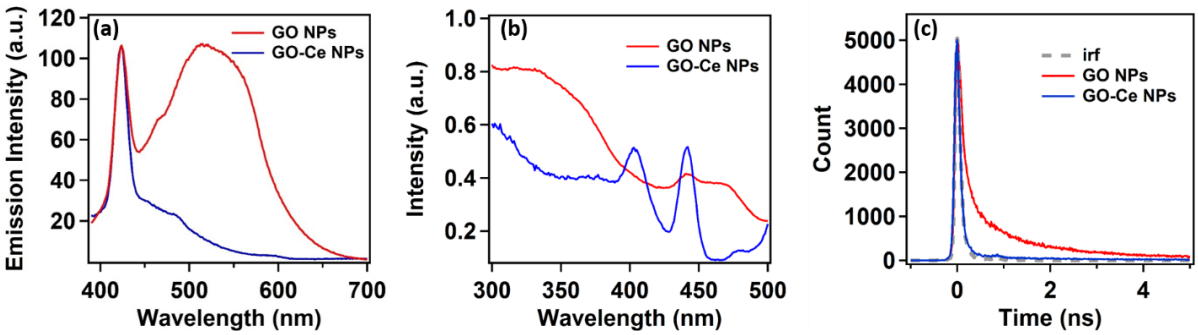

Figure 2. *(a) Longer Wavelength Photoluminescence spectra of GO NPs and GO-Ce NPs exciting at 375 nm. (b) Excitation spectra of GO NPs and GO-Ce NPs collected at 530 nm. (c) Time resolved photoluminescence of GO NPs and GO-Ce NPs (530 nm* photoluminescence *decays). Excitation wavelength is 375 nm.*

Experimental observations enable us to conclude a mechanism involving photoinduced reduction of non emissive Ce (IV) to form luminescent Ce (III) accompanied with energy pumping of cerium by photoexcited GO NPs in the structurally ordered GO-Ce nanoparticles. Again, the interaction between the cerium ions and the oxygen containing functional groups of GO leads to decoupling of the functional groups and there by weakens the intensity of luminescence originated from disordered induced defect states which results a non radiative chanel to generate trivalent cerium via single electron transfer from the orbitals of the functional groups to the vacant 4f orbitals of tetravalent cerium.

3.2.2. Optical sensing by GO-Ce NPs:

Cerium doped graphene oxide nano particles (GO-Ce NPs) shows high photoluminescence intensity. The characteristic maximum emission spectra of GO-Ce NPs at 350nm (λex =255nm) which was attributed to the 5d-4f transitions of Cerium ions. The large overlap of emission spectra of PA and absorption spectra of GO-Ce NPs indicates the energy transfer process follows the resonance energy transfer (RET) mechanism in addition to photo induced electron transfer (PET), which alone cannot give such a remarkable high flourescence quenching. The objective of our work is to investigate a NPs based strategy for the sensitive and selective determination of explosive nitro compound specially 2,4,6-tri-nitro phenol (known as Picric acid) in aqueous media and to develop a rapid, robust, simple and efficient assay with the long term goal of achieving a new analytical technology.

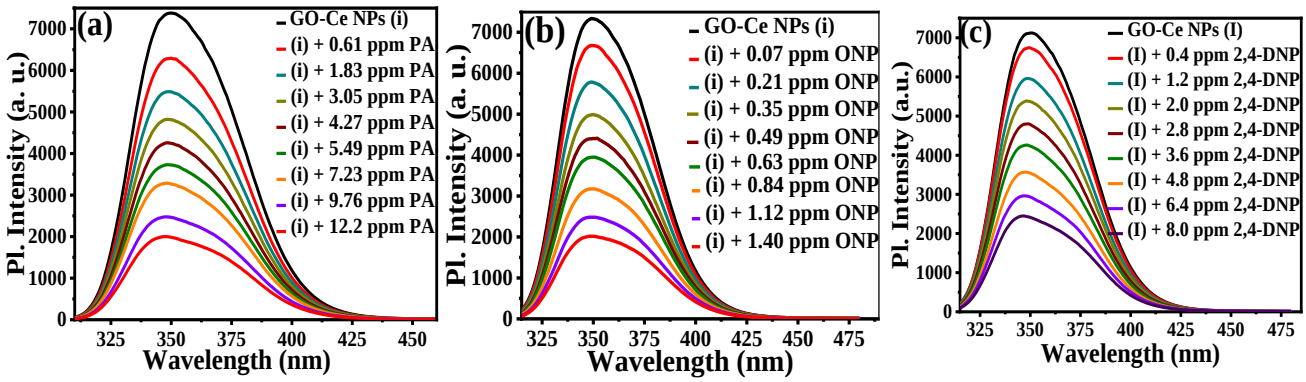
(a)
GO-Ce NPs (i)
(i) + 0.61 ppm PA
(i) + 1.83 ppm PA
(i) + 3.05 ppm PA
(i) + 4.27 ppm PA
(i) + 5.49 ppm PA
(i) + 7.23 ppm PA
(i) + 9.76 ppm PA
(i) + 12.2 ppm PA
Pl. Intensity (a. u.)
Wavelength (nm)
(b)
GO-Ce NPs (i)
(i) + 0.07 ppm ONP
(i) + 0.21 ppm ONP
(i) + 0.35 ppm ONP
(i) + 0.49 ppm ONP
(i) + 0.63 ppm ONP
(i) + 0.84 ppm ONP
(i) + 1.12 ppm ONP
(i) + 1.40 ppm ONP
Pl. Intensity (a. u.)
Wavelength (nm)
(c)
GO-Ce NPs (I)
(I) + 0.4 ppm 2,4-DNP
(I) + 1.2 ppm 2,4-DNP
(I) + 2.0 ppm 2,4-DNP
(I) + 2.8 ppm 2,4-DNP
(I) + 3.6 ppm 2,4-DNP
(I) + 4.8 ppm 2,4-DNP
(I) + 6.4 ppm 2,4-DNP
(I) + 8.0 ppm 2,4-DNP
Pl. Intensity (a.u.)
Wavelength (nm)

Figure 3. *(a) Photoluminescence spectra of GO-Ce NPs exciting at 250 nm in presence of PA. (b) Photoluminescence spectra of GO-Ce NPs exciting at 250 nm in presence of ONP. (c) Photoluminescence spectra of GO-Ce NPs exciting at 250 nm in presence of 2,4-DNP.*

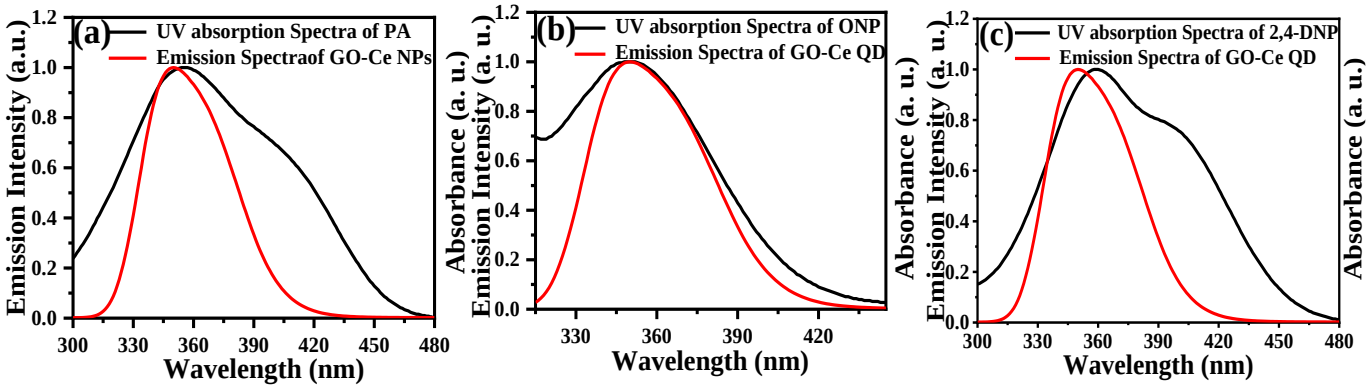

Figure 4. *(a)Overlapping spectra of photoluminescence emission spectra of GO-Ce NPs and Absorption spectra of PA. (b) Overlapping spectra of photoluminescence emission spectra of GO-Ce NPs and Absorption spectra of ONP. (c) Overlapping spectra of photoluminescence emission spectra of GO-Ce NPs and Absorption spectra of 2,4-DNP.*

3.2.3. Tuning of Photoluminescence of GO Derivatives: Effect of Solvent (Water):

To investigate the interaction among the graphene oxide layers by involving surface functional groups, photoluminescence (PL) from graphene oxide (GO) and hydroxyl enriched graphene oxide quantum dots (OH-GO QD) in UV-visible region is studied, all the optical properties have been investigated varying the concentration of OH-GO QDs in water. Like GO, OH-GO QDs also have a very broad absorption spectrum without any distinct feature. At different concentrations the spectral features remain same except the absorbance. However, a small hump near 240 nm is visible from the absorption spectra, which can be attributed to the π–π^* transition of sp^2 network. However, photoluminescence spectra of OH-GO suspension in water shows two PL maxima at ~350 nm and 440 nm when it is excited at 240 nm even at very low concentration (0.005 mg/L). Interestingly, the intensity of the PL peak cantered at 440 nm is enhanced with concentration whereas exactly opposite scenario is observed for the PL peak centred at 350 nm, clearly indicating involvement of two emissive species (species A with PL max at 350 nm and species B with PL max at 440 nm). At higher concentration, the emissive species A gets converted to a new species B which emits at 440 nm. Rather we can say that the formation of species B is favourable from species A at higher concentration. To check this conversion of species A to B is photo-driven process or a ground state phenomenon, we further recorded the excitation spectra at two extreme concentrations from two different emissive centres (350 nm and 440 nm). Excitation spectra of A (collected at PL 350 nm) is completely

different than the excitation spectra of B (collected at PL 440 nm) pointing the fact that the conversion of A to B is a ground state process. Like GO, here also we do not see any change in excitation spectra for a particular emission wavelength at different concentration and the percentage of A and B differs at higher concentration. Now we have to explore origin of species B and its structure. We have checked the PL spectra of OH-GO QD at different pH in relatively lower concentration (0.01 mg/L) The PL spectra of OH-GO QD is found to be markedly changed on switching the pH level from acidic to basic. At lower pH (~3) the predominantly existing species is found to be A with PL maxima at around 350 nm. At neutral pH the PL spectra of OH-GO QD consisting of two distinct PL maxima with predominantly of species B having PL maxima 440 nm. Going to the higher pH level the feature of the PL spectra remains almost same except the intensity, which turns out to be less than PL intensity in the neutral pH. This important observation firmly concludes two facts. Firstly, the conversion of A to B is highly dependent on the pH of the medium. Secondly, the formation of B is favourable at neutral pH. The possibility of B as a ground state proton transfer species is nullified as the formation of B in basic pH is less favoured over neutral pH. The hydrogen bonding may play a crucial role in the formation of the species B as hydrogen bonding formation is most favourable at neutral pH condition. At relatively higher concentration the formation of aggregates is one of the most common features in the nanomaterials. As OH-GO QD consisting of high density of surface hydroxyl functional groups, there is a high possibility of forming OH-GO QD aggregates through the hydrogen bonding between the layers and formation is much more facile at higher concentration.

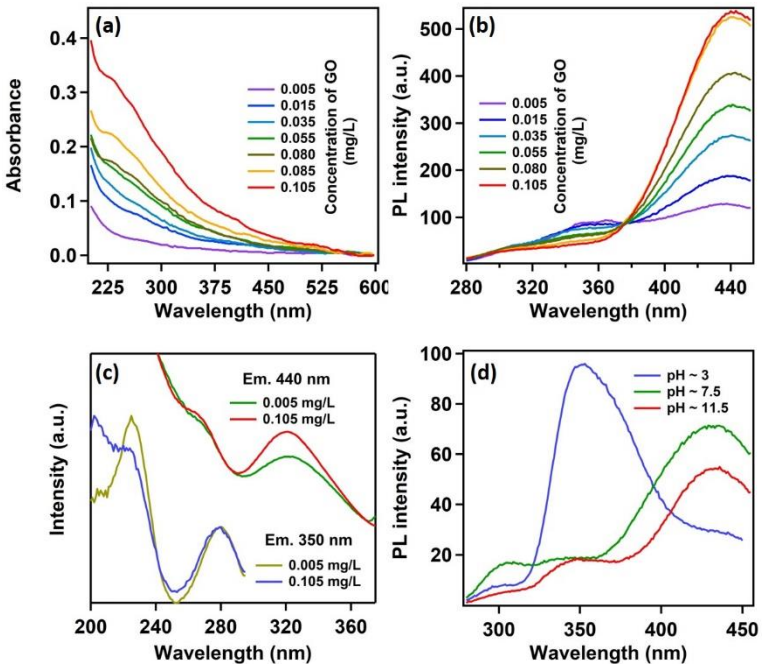

Figure 5. *Concentration dependent optical studies of OH-GO QDs. a) Concentration dependent absorption of OH-GO QDs suspension in water; b) Concentration dependent photoluminescence of OH-GO QDs suspension in water. Excitation wavelength is 240 nm; c) Excitation spectra of OH-GO QDs suspension at two extreme concentrations 0.005 mg/L and 0.105 mg/L. (monitored at two different wavelengths, lower part of the figure contains excitation spectra from emission wavelength 350 nm and upper part of the figure contains excitation spectra from emission wavelength 440 nm); d) PL spectra of OH-GO QDs at three different pH (excitation wavelength is 240 nm and concentration of OHGO QDs is 0.01 mg/L).*

Tuning of PL is observed by varying the concentration of aqueous dispersion of OH-GO QD, obtained by strong alkaline treatment on graphene oxide (GO). Hydroxyl functional groups at the surface of OH-GOQD facilitate the formation of aggregates through hydrogen bonding involving solvent water molecules and the PL band in the visible region may be originated from such aggregates. With increase in concentration of OH-GO QD in the aqueous medium, contribution of the visible PL band is markedly increased along with the decrease in the PL band in UV region. The time resolved study indicates the possibility of energy transfer from fluorophore centre of the GO layers to the aggregates and this may be responsible for the marked enhancement of the visible band of the PL spectra of OH-GOQD at high concentration.

3.2.4. Effect of Temperature on Photoluminescence of GO-PANI Nanocomposite:

The effect of temperature on the photoluminescence characteristics of synthesised GO-PANI nanocomposite at three different pH have been studied to investigate the origin of the tuneable photoluminescence bands. Experimental observation suggests that the intensity of the luminescence due to charge transfer interaction between GO and PANI, dominant at the acidic pH, dependent on layer-to-layer stacking and the hydrogen bonding interaction between GO and PANI, is found to be temperature dependent and related to the transition from π^* to π and σ^* to n. Since the structural order of the nanocomposite varies with temperature, the luminescence behaviour may be controlled by temperature, specially at the pH≈6.

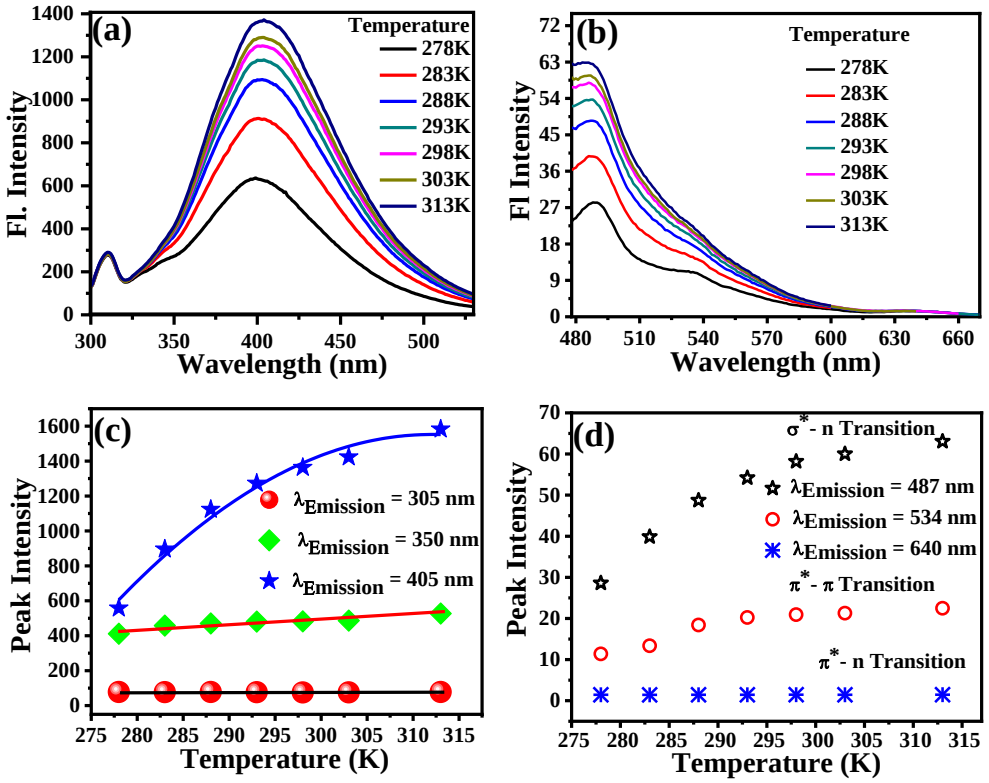

Figure 6. *Temperature dependent optical studies of GO-PANI nanocomposite. a) Temperature dependent photoluminescence emission spectra of GO-PANI nanocompositesuspension in water;Excitation wavelength is 280 nm. b) Temperature dependent photoluminescence emission spectra of GO-PANI nanocomposite suspension in water;Excitation wavelength is 420 nm. c) Emission intensity vs temperature diagram of GO-PANI nanocomposite (monitored at three different wavelengths of photoluminescence emission spectra, 305 nm, 350 nm and 405 nm). d) Emission intensity vs temperature diagram of GO-PANI nanocomposite (monitored at three different wavelengths of photoluminescence emission spectra, 487 nm, 534 nm and 640 nm).*

In the pH 6 with the increase in temperature the intensity increases and saturation occurs at 298 and 303K , upon 280 and 420 nm excitation the change in intensity remain in same pattern. The charge transfer interaction is the resultant effect of the σ*-n, π*-π transition ,with the increase in temperature orderness of the structure increases i,e the packing between PANI&GO increases. Interaction between PANI &GO moiety, electrostatic, hydrogen bonding and π-π stacking with increase interms of charge transfer the charge transfer complex form due to σ*-n,π-π* transition. It also proves that the interaction occurs in the ground state due to change in interaction spectra.

3.2.5. Photoluminescence of Graphitic Carbon Nitride: Effect of pH and Interaction with GO:

We have synthesised graphitic carbon nitride (g-CN_X) to study its photoluminescence characteristics at three different pH to explore the origin of the photoluminescence bands. Experimental observation reveals that protonation-deprotonation on the nitrogen atoms in the graphitic carbon nitride play an important role to the intensity of the defect induced luminescence band. In addition to this, the photoluminescence of graphitic carbon nitride is found to be modulated by graphene oxide (GO) possibly due to the interaction between GO and g-CN_X.

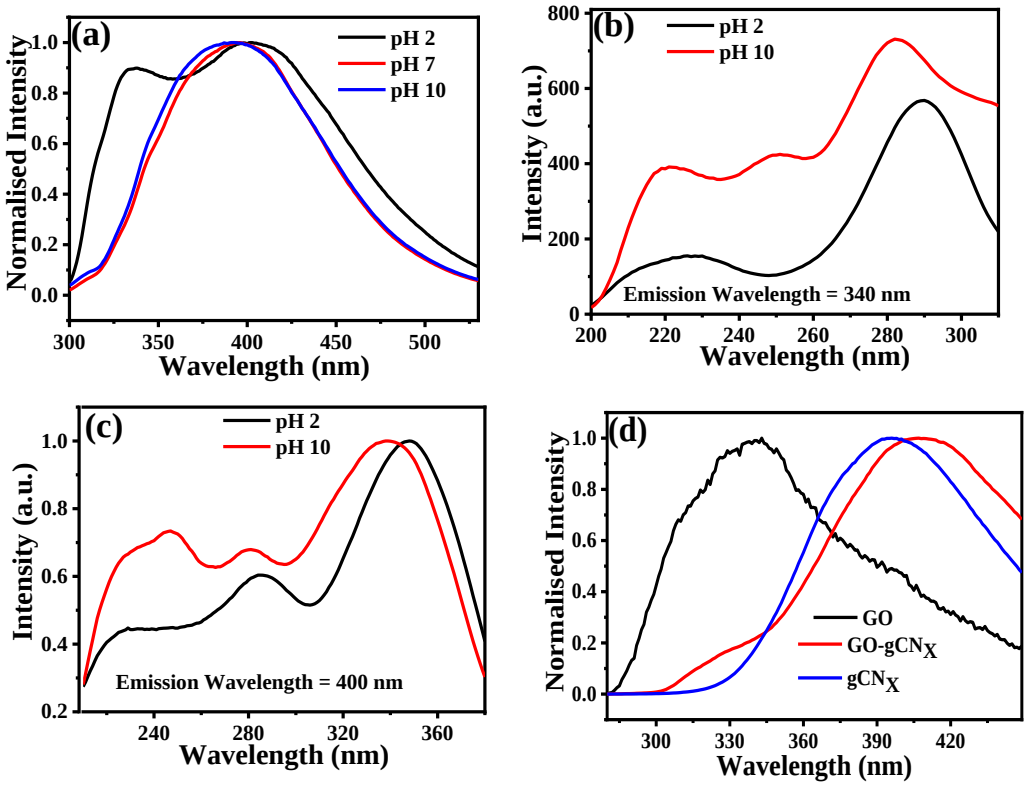

Figure7. *a) pH dependent photoluminescence emission spectra of g-CNx, suspension in water;Excitation wavelength is 280 nm. b) pH dependent photoluminescence excitationspectra of g-CNx suspension in water;Emission wavelength monitored at340 nm; c) pH dependent photoluminescence excitationspectra of g-CNx suspension in water; Emission wavelength monitored at400 nm d) PL spectra of GO, g-CNx and GO-g-CNx.*

Fig.7ashows the emission spectra of graphitic carbon nitride with the variation of different pH (2,7 and 10). Plot of the normalised Intensity vs wavelength (nm), indicates two peaks at pH = 2, one at about 338 nm and another at 405 nm. At pH = 7 and 10, the emission maximum is obtained at around 395 nm.The red shifted emission around 400-420 nm is attributed as the emission from defect induced states which are generated by the excitonic transitions resulting electrons in the defect states located below the conduction band. Excitation spectra of g-CN_X monitored at the wavelength of 340 nm shows the absence of a peak around 250 nm at pH = 2 (Fig. 7b) and this observation clearly indicates a structural change at low pH may be due to the protonation at the nitrogen centers. Excitation spectra monitored at 400 nm (Fig 7c) also supports the fact.We have also studied the photoluminescence of g-CN_X in presence of GO and Fig. 7d shows the normalised luminescence spectra of GO, g-CN_X and g-CN_X in presence of

GO. The slight red shift of the luminescence band of g-CN_X in presence of GO is suggesting the formation of a complex where the GO moiety decreases the effective band gap of g-CN_X.

3.2.6. Photoluminescence modulation of Graphene Oxide (GO) in presence of Pluronic F-127 Copolymer:

Photoluminescence of graphene oxide (GO) is markedly affected by a co-polymer Pluronic F-127 (PF-127), in both acidic and alkaline medium. In the acidic medium (pH ≈ 2), the anchor-buoy-type adsorption of the PF-127 on the GO sheets creates a non-polar environment around the fluorophoric moiety of GO. In consequence, solvent relaxation is hindered and interlayer separation of GO is increased. This results a marked 45 nm blue shift by exciting the sample at 240 nm and 38 nm blue shift by exciting the sample at 280 nm of photoluminescence spectrum. In alkaline medium (pH ≈ 10), the electrostatic repulsion between negatively charged carboxylate ions at the GO edges does not favour such PF-127 adsorption and further separation between the GO sheets is not pronounced. This leads to small blue shift in the photoluminescence band. But, the enhancement in fluorescence intensity of a new luminescence band at 305 nm, in the presence of PF-127 (at pH ≈ 10), is possibly due to weakening of π-π stacking interaction by the intercalation of PF-127 within the basal planes of GO. This type of PF-127 intercalated largely separated GO layers may be responsible for the fluorescence at 305 nm.

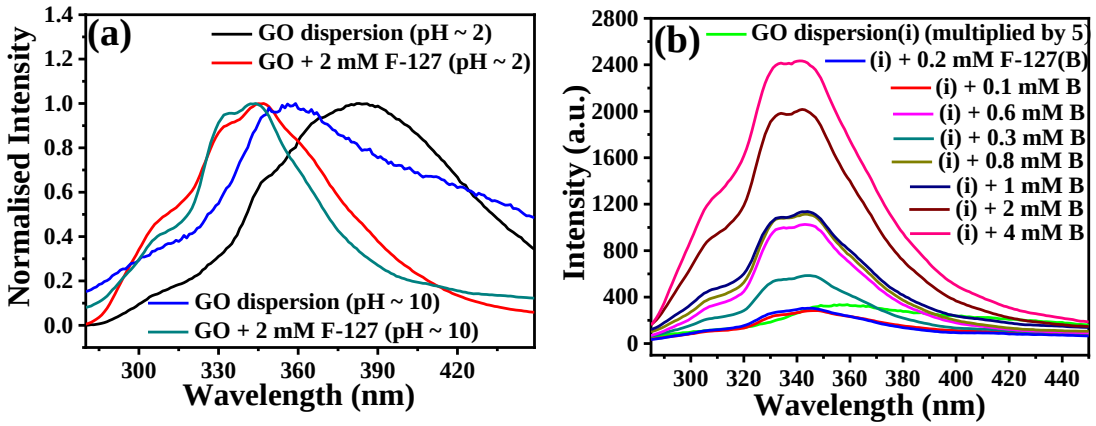
(a)
GO dispersion (pH ~ 2)
GO + 2 mM F-127 (pH ~ 2)
GO dispersion (pH ~ 10)
GO + 2 mM F-127 (pH ~ 10)
Normalised Intensity
Wavelength (nm)
(b)
GO dispersion(i) (multiplied by 5)
(i) + 0.2 mM F-127(B)
(i) + 0.1 mM B
(i) + 0.6 mM B
(i) + 0.3 mM B
(i) + 0.8 mM B
(i) + 1 mM B
(i) + 2 mM B
(i) + 4 mM B
Intensity (a.u.)
Wavelength (nm)

Figure8. *a) pH dependent photoluminescence emission spectra of GO in presence of F-127.b) Photoluminescence emission spectra of GO in presence of F-127 at pH 10.*

4. Conclusion

The entire work is devoted to the synthesis of graphene based and carbon based nanomaterials and study of their photoluminescence property in presence of heavy metal ions, macromolecules etc. at different experimental condition. we have synthesized cerium incorporated GO NPs (GO-Ce NPs) by a simple one pot synthetic method and characterized it by several techniques. GO-Ce NPs exhibit much more ordered and defect free structure in comparison to GO NPs and shows more than 100-fold amplification of the photoluminescence intensity in GO-Ce NPs compared to GO. Our mechanistic investigation reveals that photoinduced reduction of Ce (IV) to emissive Ce (III) by the GO moiety with the involvement of defect states originated by oxygen containing functional groups followed by energy transfer from the photoexcited GO as the origin of such photoluminescence amplification. Using GO-Ce NPs as a fluorophore, we successfully demonstrate the detection of the nitro compounds in aqueous medium. The photoluminescence study of OH enriched GO QDs (OH-GO QDs) in different concentration indicates the enhancement of a band in visible region due to the formation of aggregates through h-bonds by involving solvent water molecules. Investigation of the effect of temperature on the photoluminescence spectra of synthesised GO-PANI nanocomposites suggests the role of charge transfer on the photoluminescence modulation of GO-PANI nanocomposite. Photoluminescence study of g-CNx in presence of GO shows the interaction between the two nanomaterials and possibilities of energy transfer affecting the photoluminescence features. The change in photoluminescence band of GO with the interaction with a triblock copolymer PF-127, in aqueous solutions is attributed to the formation of a new materials having interesting photoluminescence characteristics.

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7. List of Publications

1) Photoluminescence Amplification of Cerium Incorporated Graphene Oxide Nanoparticles by Photoinduced Reduction: A Mechanistic Study Highlighting Structural Orderness. **Pyne, D, K.**; Chatterjee, S.; Biswas, T; Saha, P; Dutta, P; Halder, A.; Journal of Luminescence, **2021**, 235, 118019.
2) Tunable Luminescence of a synthesised furophenanthraquinone derivative: Interactions with different solvents. Sarkar, A.; **Pyne, D, K.**; Biswas, T.; Das, R.; Kar, G, K.; Halder, A., Luminescence: The Journal of Biological and Chemical Luminescence, **2020**, 35,709.
3) Tunable luminescence of graphene oxide-polyaniline nano-composite: Effect of an anionic surfactant. Saha, P.; **Pyne, D. K.**; Dutta, P.; Halder, A.; Journal of Luminescence, **2019**, 206, 218.
4) Photoluminescence of Graphene Oxide: Effect of pH, Surfactant and Polymer. **Pyne, D, K.;** Saha, P.; Halder, A., EPA News Letter, **2018**, 94, 11.
5) Effect of an anionic surfactant (SDS) on the photoluminescence of graphene oxide (GO) in acidic and alkaline medium. Saha, P.; **Pyne, D. K.**; Ghosh, S.; Banerjee, S.; Das, S.; Ghosh, S.; Dutta, P.; Halder, A., RSC Advances, **2018**, 8, 584.

6) pH dependent tunable photoluminescence of Polyaniline grafte Graphene Oxide (GO–PANI) nanocomposite. Saha, P.; **Pyne, D. K.;** Pal, M.; Datta, S.; Das, P. K.; Dutta, P.; Halder, A. Journal of Luminescence, **2017**, 181, 138.

8. Presentation of the work in different seminars, symposiums, conferences

1. Attended the “International Conference on Current Trends in Materials Science and Engineering (CTMSE 2018)” Dated: January 19-20,2018 Organized by IEM Kolkata and S.N.Bose National Centre for Basic Sciences, Kolkata, West Bengal. (Copy Attached)
2. Attended the “Two Day regional Symposium” Dated:January 04-05, 2018, Organized by Department of Chemistry, Presidency University, Kolkata, West Bengal. (Copy Attached)

3. Attended the “International Symposium on Recent Advances in Chemistry and Material Sciences(2019)” Dated: August 02-03, 2019, Organized by Indian Chemical Society, West Bengal. (Copy Attached)

4. Attended the “International seminar on Recent Advances in Chemistry& Material Sciences-2020 (RACMS-2020)” Dated: August 2-3, 8,15,22&29, 2020, Organized by Indian Chemical Society, West Bengal. (Copy Attached)

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